Dioxygen-Coupled Oxidative Amination of Styrene

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Supporting Information

Experimental Section

General Methods. ^1H NMR spectral data were obtained using Bruker AC 250, AC 300, or AM 360 MHz spectrometers. The chemical shifts (δ) are given in parts per million relative to internal TMS (0 ppm for ^1H) or CDCl_3 (77 ppm for ^{13}C). GC analyses were carried out with GC-17A Shimadzu gas chromatograph, column HP/Rtx-5 (crossbond 5% diphenyl – 95% dimethyl polysiloxane), 15 m, 0.25 mm ID, column temperature: 150 °C for 1min, 310 °C (40 °C/min). GC-MS analyses were carried out with GC-17A Shimadzu setup linked to an QP-5000 mass spectrometer. Column chromatography (Merck silica gel 60; 230 – 400 mesh) was performed with an appropriate ratio of EtOAc/Hexane mixed solvent.

Anhydrous 1,2-dimethoxyethane (Aldrich), 2-oxazolidinone (Aldrich), 2-pyrrolidinone (Aldrich), *p*-toluenesulfonamide (Aldrich), (S)-(-)-4-benzyl-2-oxazolidinone (Aldrich), (S)-(-)-4-isopropyl-2-oxazolidinone (Aldrich), styrene (Aldrich), 4-(trifluoromethyl)styrene (Aldrich), 4-methylstyrene (Aldrich), 4-chlorostyrene (Aldrich), Indene (Aldrich), 2-vinylnaphthalene (ACROS), 1,2-dihydronaphthalene (Aldrich), 4-fluorostyrene (Aldrich), 4-vinylanisole, triethylamine (Aldrich), PdCl_2 (Johnson Matthey), anhydrous CuCl_2 (Aldrich), anhydrous sodium acetate (Mallinckrodt AR), tetrabutylammonium acetate (Aldrich), palladium(II) acetate (Aldrich), deuterium oxide (Aldrich), and oxygen gas (BOC) were used as received. Deuterated THF was distilled from purple sodium/benzophenone ketyl solution prior to use. L_2PdCl_2 (L = MeCN or PhCN) were prepared by literature procedures.¹

Representative Procedure for the Palladium-Catalyzed Oxidative Amination of Styrene (Table 1, entry 1). The reaction conditions and results are summarized in Tables 1 and 2. A typical procedure is given for the reaction of entry 1, Table 2. $(\text{MeCN})_2\text{PdCl}_2$ (6.5 mg, 0.025 mmol), CuCl_2 (3.4 mg, 0.025 mmol), Et_3N (7.0 μL , 0.05 mmol) and 2-oxazolidinone (43.6 mg, 0.501 mmol) in DME (2 mL) were suspended in a 13x100 mm disposable culture tube. The reaction tube was placed into a custom 48-well parallel reactor mounted in a Large Capacity Mixer (Glas-Col) and the headspace was purged with molecular oxygen for ca. 30 min. After warming to 60 °C, styrene (0.34 mL, 3.0 mmol) was added to initiate the reaction. The reaction was carried out for 24 h under an oxygen atmosphere (1.1 atm). For product purification, the reaction mixture was adsorbed onto silica gel and isolated by eluting with ethyl acetate/hexanes (20:80 to 50:50) to give 93.5 mg (99% yield) of 3-(1-phenylvinyl)-oxazolidin-2-one (**II**). Reactions performed in flasks equipped with magnetic stirring bars, required vigorous

bubbling of oxygen gas through the solution to result in comparable yields of product formation.

Table S1: (CH₃CN)₂PdCl₂-catalyzed oxidative amination of styrenes by 2-oxazolidinone (HN^{ox}).

	<i>p</i> -XC ₆ H ₄ CH=CH ₂	Product	% Yield (aME : MA) ^b
1	X = H	aME	77
2 ^c	CF ₃	aME	40
3	Cl	aME	36
4	F	aME + MA	89 (11.5:1)
5 ^c	CH ₃	aME + MA	56 (8:1)
6 ^c	OCH ₃	MA	51

^aReaction conditions: Olefin (3 mmol), HN^{ox} (0.5 mmol), (CH₃CN)₂PdCl₂ (0.025 mmol), CuCl₂ (0.025 mmol), 1 atm O₂, 2 mL DME, 60 °C, 24 h. ^b¹H NMR spectroscopy, Ph₃CH as the internal standard. ^cOlefin (0.5 mmol).

3-((*E*)-Styryl)-oxazolidin-2-one (I**).** Column chromatography (EtOAc/hexane, 0:100 to 40:60) afforded spectroscopically pure **I** in the form of pale yellow crystals. ¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, 1H, *J* = 14.7 Hz), 7.33-7.19 (m, 5 H), 5.77 (d, 1 H, *J* = 14.7 Hz), 4.51 (t, 2H, *J* = 8.1 Hz), 3.86 (t, 2H, *J* = 8.1 Hz); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 155.38, 135.78, 128.69, 128.64, 126.62, 125.45, 123.91, 111.00, 62.24, 42.45; MS: *m/z* (EI): 189 (M⁺, 100), 144 (38), 130 (91), 117 (23), 103 (54), 89 (17), 77 (41), 65 (21), 51 (35). NMR data for **I** have been reported previously.³

3-(1-Phenylvinyl)-oxazolidin-2-one (II**).** Column chromatography (EtOAc/hexane, 0:100 to 50:50) and evaporation of solvent afforded the pale yellow oil **II**. ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.33 (m, 5H), 5.24 (s, 1 H), 5.21 (s, 1 H), 4.38 (t, 2 H, *J* = 7.8 Hz), 3.73 (t, 2 H, *J* = 7.8 Hz); ¹³C{¹H} (75 MHz, CDCl₃) δ 156.04, 143.15, 135.94, 128.87, 128.52, 126.79, 106.78, 61.85, 46.49; MS: *m/z* (EI): 189 (M⁺, 58), 188 (46), 144 (17), 130 (23), 117 (12), 104 (43), 103 (100), 102 (18), 91 (23), 78 (20), 77 (75), 51 (40), 50 (14), 42 (16), 39 (17).

3-[(*E*)-2-(4-Chlorophenyl)-vinyl]-oxazolidin-2-one (III**).** Column chromatography (EtOAc/hexane, 0:100 to 50:50) and evaporation of solvent afforded white crystals of **III**. ¹H NMR (300 MHz, CDCl₃) δ 7.35 (d, 1H, *J* = 14.7 Hz), 7.27-7.25 (m, 4H), 5.72 (d, 1H, *J* = 14.7 Hz), 4.51 (t, 2H, *J* = 8.1 Hz), 3.84 (t, 2H, *J* = 8.1 Hz); ¹³C{¹H} NMR (75 MHz,

CDC1₃) δ 155.29, 134.40, 132.15, 128.84, 126.63, 124.50, 109.78, 62.26, 42.45; MS: m/z (EI): 223 (M⁺, 100), 178 (20), 166 (33), 164 (99), 144 (22), 137 (34), 116 (12), 102 (34), 89 (27), 71 (22), 59 (57), 43 (68).

III

3-[1-(4-Chlorophenyl)-vinyl]-oxazolidin-2-one (IV). Column chromatography (EtOAc/hexane, 0:100 to 40:60) and evaporation of solvent afforded the pale yellow oil **IV**. ¹H NMR (300 MHz, CDC1₃) δ 7.32 (s, 4 H), 5.18 (s, 1 H), 5.16 (s, 1 H), 4.42 (t, 2 H, J = 7.9 Hz), 3.78 (t, 2 H, J = 7.9 Hz); ¹³C {¹H} NMR (75 MHz, CDC1₃) δ 155.80, 142.46, 134.56, 130.83, 128.80, 128.22, 106.55, 61.93, 46.54; MS: m/z (EI): 223 (M⁺, 68), 222 (29), 188 (39), 178 (13), 164 (21), 144 (19), 137 (80), 125 (26), 102 (59), 89 (11), 75 (48), 63 (13), 51 (40), 42 (22).

IV

3-((E)-2-*p*-Tolylvinyl)-oxazolidin-2-one (V). Column chromatography (EtOAc/hexane, 0:100 to 40:60) afforded white crystals of **V**. ¹H NMR (300 MHz, CDC1₃) δ 7.33 (d, 1H, J = 14.7 Hz), 7.27-7.09 (m, 4 H), 5.75 (d, 1 H, J = 14.7 Hz), 4.47 (t, 2 H, J = 8.1 Hz), 3.82 (t, 2 H, J = 8.1 Hz), 2.32 (s, 3 H); MS: m/z (EI): 203 (M⁺, 100), 158 (26), 144 (94), 131 (16), 115 (41), 103 (11), 91 (29), 78 (44), 65 (15), 51 (19), 41 (20). ¹³C {¹H} NMR (75 MHz, CDC1₃) δ 152.03, 137.78, 136.64, 129.62, 129.51, 127.15, 123.39, 111.27, 62.10, 40.19.

V

3-(1-*p*-Tolylvinyl)-oxazolidin-2-one (VI). Column chromatography (EtOAc/hexane, 0:100 to 40:60) and evaporation of solvent afforded the pale yellow oil **VI**. ¹H NMR (300 MHz, CDC1₃) δ 7.29-7.16 (m, 4H), 5.22 (s, 1H), 5.20 (s, 1H), 4.41 (t, 2H, J = 7.9 Hz), 3.75 (t, 2H, J = 7.9 Hz), 2.36 (s, 3H); ¹³C {¹H} NMR (75 MHz, CDC1₃) δ 156.15, 143.15, 138.95, 133.16, 129.34, 126.81, 106.32, 61.88, 46.63, 21.41; MS: m/z (EI): 203 (M⁺, 27), 188 (17), 144 (12), 118 (10), 117 (29), 115 (21), 105 (9), 91 (15), 65 (10), 51 (6), 39 (14).

VI

3-(1-*p*-Tolylethyl)-oxazolidin-2-one (VII). Column chromatography (EtOAc/hexane, 0:100 to 40:60) and evaporation of solvent afforded the white crystals of **VII**. ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.09 (m, 4H), 5.18 (q, 1H, $J = 7.0$ Hz), 4.24 (m, 2H), 3.47 (m, 1H), 3.14 (m, 1H), 2.34 (s, 3H), 1.56 (d, 3H, $J = 7.0$ Hz); MS: m/z (EI): 205 (M^+ , 39), 190 (77), 146 (19), 119 (100), 103 (10), 91 (48), 77 (20), 65 (25), 51 (17), 41 (32). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 152.27, 133.12, 129.62, 129.51, 129.30, 125.58, 62.46, 51.39, 42.74, 21.28, 16.56.

VII

3-[(*E*)-2-(4-Trifluorophenyl)-vinyl]-oxazolidin-2-one (VIII). Column chromatography (EtOAc/hexane, 1:2) and evaporation of solvent afforded yellow-white crystals of **VIII**. ^1H NMR (300 MHz, CDCl_3) δ 7.55-7.39 (m, 5H), 5.78 (d, 1H, $J = 14.7$ Hz), 4.53 (t, 2H, $J = 8.1$ Hz), 3.87 (t, 2H, $J = 8.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 155.28, 140.19, 125.97, 125.69, 125.64, 125.48, 109.47, 62.34, 42.39; MS: m/z (EI): 257 (M^+ , 74), 212 (22), 198 (100), 171 (29), 151 (44), 102 (10), 89 (10), 74 (11), 51 (13).

VIII

3-[1-(4-Trifluoromethylphenyl)-vinyl]-oxazolidin-2-one (IX). Column chromatography (EtOAc/hexane, 0:100 to 40:60) and evaporation of solvent afforded the pale yellow oil **IX**. ^1H NMR (300 MHz, CDCl_3) δ 7.63 – 7.50 (m, 4H), 5.22 (s, 1H), 5.21 (s, 1H), 4.45 (t, 2H, $J = 7.7$ Hz), 3.82 (t, 2H, $J = 7.7$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 155.73, 142.53, 139.73, 129.78, 127.30, 125.61, 125.55, 107.25, 62.01, 46.51; MS: m/z (EI): 257 (M^+ , 86), 256 (22), 238 (12), 212 (27), 198 (33), 188 (59), 172 (58), 171 (95), 159 (22), 151 (100), 145 (18), 116 (11), 103 (48), 102 (25), 95 (11), 75 (21), 69 (16), 51 (23), 50 (22), 42 (80), 41 (31).

IX

3-[(E)-2-(4-Fluorophenyl)-vinyl]-oxazolidin-2-one (X). Column chromatography (EtOAc/hexane, 0:100 to 50:50) and evaporation of solvent afforded white crystals of **X**. ^1H NMR (300 MHz, CDCl_3) δ 7.31 (d, 1H, $J = 14.7$ Hz), 7.29-7.25 (m, 2H), 7.02-6.96 (m, 2H), 5.74 (d, 1H, $J = 14.7$ Hz), 4.50 (t, 2H, $J = 8.1$ Hz), 3.83 (t, 2H, $J = 8.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 163.57, 159.66, 131.88, 126.92, 126.80, 123.75, 115.75, 115.40, 109.90, 62.24, 42.44; MS: m/z (EI): 207 (M^+ , 100), 162 (25), 148 (97), 135 (23), 121 (55), 107 (19), 101 (47), 81 (21), 74 (21), 57 (14), 51 (11), 44 (11).

X

3-[1-(4-Fluorophenyl)-vinyl]-oxazolidin-2-one (XI). Column chromatography (EtOAc/hexane, 0:100 to 40:60) and evaporation of solvent afforded the pale yellow oil **XI**. ^1H NMR (300 MHz, CDCl_3) δ 7.38 – 7.34 (m, 2H), 7.07 – 7.04 (m, 2H), 5.16 (s, 1H), 5.13 (s, 1H), 4.41 (t, 2H, $J = 7.6$ Hz), 3.77 (t, 2H, $J = 7.6$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 165.04, 161.10, 142.44, 132.16, 128.73, 128.59, 115.68, 115.33, 106.12, 61.88, 46.53; MS: m/z (EI): 207 (M^+ , 62), 206 (44), 162 (19), 148 (27), 135 (11), 122 (45), 121 (100), 120 (18), 109 (27), 101 (63), 95 (16), 75 (29), 51 (14), 50 (13), 42 (25), 41 (16).

XI

3-[1-(4-Fluorophenyl)-ethyl]-oxazolidin-2-one (XII). Column chromatography (EtOAc/hexane, 0:100 to 50:50) and evaporation of solvent afforded white crystals of **XII**. ^1H NMR (300 MHz, CDCl_3) δ 7.29-7.25 (m, 2H), 7.02-6.96 (m, 2H), 5.20 (q, 1H, $J = 7.0$ Hz), 4.27 (m, 2H), 3.49 (m, 1H), 3.14 (m, 1H), 1.57 (d, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 155.35, 128.71, 128.59, 123.72, 115.63, 115.29, 61.86, 50.78, 39.87, 16.45; MS: m/z (EI): 209 (M^+ , 40), 194 (60), 150 (21), 123 (100), 103 (65), 95 (15), 75 (30), 68 (13), 42 (23).

XII

3-(1*H*-Inden-1-yl)-oxazolidin-2-one (XIII) Column chromatography (EtOAc/hexane, 0:100 to 30:70) and evaporation of solvent afforded yellow crystals of **XIII** (24%). ^1H NMR (300 MHz, CDCl_3) δ 7.44 – 7.21 (m, 4H), 6.91 – 6.89 (m, 1H), 6.31 – 6.29 (m, 1H), 5.62 (m, 1H), 4.33 – 4.26 (m, 2H), 3.22 – 3.14 (m, 1H), 3.06 – 2.98 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 134.88, 133.74, 128.80, 126.42, 123.76, 122.02, 62.39, 60.76, 40.70. ESI [M^+] = 201.0102.

XIII

3-[1-(2-Naphthyl)-vinyl]-oxazolidin-2-one (XIV) Column chromatography (EtOAc/hexane, 20:80 to 40:60) and evaporation of solvent afforded yellow crystals of **XIV**. ^1H NMR (300 MHz, CDCl_3) δ 7.83 – 7.80 (m, 4H), 7.47 - 7.44 (m, 3H), 5.29 (d, 2H, $J = 7.7$ Hz), 4.35 (t, 2H, $J = 7.7$ Hz), 3.70 (t, 2H, $J = 7.7$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 156.09, 143.17, 133.44, 133.17, 128.31, 128.16, 127.74, 126.60, 126.54, 126.01, 124.49, 107.16, 61.87, 46.54.

XIV

3-(1,2-Dihydro-1-naphthyl)-oxazolidin-2-one (XV) Column chromatography (EtOAc/hexane, 20:80 to 40:60) and evaporation of solvent afforded light brown crystals of **XV**. ^1H NMR (300 MHz, CDCl_3) δ 7.33 – 7.10 (m, 4H), 6.54 – 6.50 (m, 1H), 6.07 – 6.01 (m, 1H), 5.25 – 5.21 (m, 1H), 4.30 – 4.13 (m, 2H), 3.52 – 3.44 (m, 1H), 3.18 – 3.10 (m, 1H), 2.76 – 2.49 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 157.88, 133.97, 131.30, 128.69, 128.18, 127.45, 126.59, 125.78, 62.20, 49.21, 41.25, 28.45; ESI [M^+] = 215.11.

XV

3-[1-(4-Methoxyphenyl)-ethyl]-oxazolidin-2-one (XVI). Column chromatography (EtOAc/hexane, 0:100 to 50:50) and evaporation of solvent afforded pale yellow crystals of **XVI**. ^1H NMR (300 MHz, CDCl_3) δ 7.27 (d, 2H, $J = 8.6$ Hz), 6.89 (d, 2H, $J = 8.6$ Hz), 5.19 (q, 1H, $J = 7.0$ Hz), 4.26 (m, 2H), 3.81 (s, 3H), 3.48 (m, 1H), 3.14 (m, 1H), 1.56 (d, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 155.70, 128.25, 113.96, 61.86, 55.27, 50.93, 39.94, 16.45; MS: m/z (EI): 221 (M^+ , 40), 206 (76), 193 (16), 162 (11), 149 (14), 135 (100), 134 (72), 119 (12), 105 (33), 91 (29), 77 (28), 65 (19), 51 (16), 42 (20).

XVI

(S)-4-Isopropyl-3-(1-phenyl-vinyl)-oxazolidin-2-one (XVII). Column chromatography (25 % EtOAc in hexanes) and evaporation of solvent afforded pure **XVII** as pale yellow crystals. ^1H NMR (CDCl_3 , 300 MHz) δ 0.78 (d, 3 H, $J = 6.9$ Hz), 0.92 (d, 3 H, $J = 6.7$ Hz), 1.88 (m, 1 H), 3.88 (dt, 1 H, $J = 8.4, 3.9$ Hz), 4.18 (dd, 1 H, $J = 5.1$ Hz), 4.39 (t, 1 H, $J = 9.3$ Hz), 5.51 (s, 1 H), 5.52 (s, 1 H), 7.39 (bs, 5 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) 156.9, 141.5, 135.8, 129.1, 128.8, 126.9, 111.9, 63.1, 56.9, 29.2, 17.7.

XVII

(S)-4-Benzyl-3-(1-phenyl-vinyl)-oxazolidin-2-one (XVIII). Column chromatography (50% EtOAc in hexanes) afforded pure **XVIII** as a pale yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ 2.65 (dd, 1 H, $J = 9.6, 4.5$ Hz), 2.98 (dd, 1 H, $J = 13.5, 2.7$ Hz), 4.12 (m, 2 H), 4.26 (m, 1H), 5.51 (s, 1 H), 5.54 (s, 1 H), 6.93 (d, 2 H, $J = 5.7$ Hz), 7.23 (m, 3 H), 7.41 (bs, 5 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) 156.3, 141.3, 135.9, 135.5, 129.2, 129.0, 128.8, 127.3, 126.9, 111.3, 66.6, 57.4, 38.8.

XVIII

2-(1-Phenyl-vinyl)-isoindole-1,3-dione (XIX). Column chromatography (50% Diethyl Ether in hexanes) and evaporation of solvent afforded pure **XIX**. ^1H NMR (CDCl_3 , 300 MHz) 5.45 (s, 1 H), 6.01 (s, 1 H), 7.37 (m, 4H), 7.7 – 7.9 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$

NMR (CDCl₃, 75 MHz) 167.3, 134.7, 134.6, 132.1, 129.2, 128.9, 125.6, 124.1, 123.8, 116.3.

XX

4-Methyl-N-(1-phenylethylidene)-benzenesulfonamide (XX). Column chromatography (EtOAc/hexane, 10:90 to 20:80) and evaporation of solvent afforded pale-yellow crystals of **XX**. ¹H NMR (300 MHz, CDCl₃) δ 7.94 – 7.88 (m, 4H), 7.54 – 7.49 (m, 1H), 7.42 – 7.32 (m, 4H), 2.97 (s, 3H), 2.43 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 179.98, 143.67, 138.86, 137.67, 133.31, 129.61, 128.75, 128.41, 127.21, 21.71, 21.27.

XX

1-(1-phenylvinyl)-pyrrolidin-2-one (XXI). Column chromatography (EtOAc/hexane, 50:50) and evaporation of solvent afforded pale-yellow crystals of **XXI**. ¹H NMR (300 MHz, CDCl₃) δ 7.33 (s, 5H), 5.40 (s, 1H), 5.29 (s, 1H), 3.54 (t, 2H, *J* = 7.0 Hz), 2.56 (t, 2H, *J* = 7.9 Hz), 2.11 (quintet, 2H, *J* = 7.5 Hz); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 174.76, 143.69, 136.35, 128.63, 128.54, 126.49, 109.47, 49.66, 32.06, 18.69.

XXI

Synthesis of (Et₃N)₂PdCl₂ (4). Et₃N (1.0 mL, 7.17 mmol) was added to a stirred suspension of (PhCN)₂PdCl₂ (300 mg, 0.778 mmol) in 15 mL benzene. After 10 min a dark red solution formed, and the solvent was then evaporated to dryness. The residue was washed with pentane and dried *in vacuo* to yield the orange product, (Et₃N)₂PdCl₂ (**2**) (0.163 g, 55%). ¹H NMR (CDCl₃, 300 MHz) 1.46 (t, *J* = 7.0 Hz, Me), 2.83 (q, *J* = 7.2 Hz, CH₂); (THF-*d*₈, δ, 360 MHz) 1.43 (t, 6 H, *J* = 6.8 Hz), 2.84 (q, 4 H, *J* = 6.8 Hz).² Crystals suitable for X-ray diffraction analysis precipitated from a toluene solution upon layering with pentane at –35 °C. (see X-ray crystallographic data below).

Control Experiments 1: Reaction of 2-Oxazolidinone with Acetophenone under catalytic conditions. Following a procedure similar to that described above for the catalytic reactions, (MeCN)₂PdCl₂ (6.5 mg, 0.025 mmol), CuCl₂ (3.4 mg, 0.025 mmol), Et₃N (7 μL, 0.05 mmol) and 2-oxazolidinone (43.6 mg, 0.5 mmol) in DME (2mL) were combined in a 13x100 mm disposable culture tube. After purging with oxygen and warming to 60 °C, acetophenone (0.35 mL, 3.0 mmol) was added to the reaction mixture and the mixture was stirred for 24 h. No 3-(1-phenylvinyl)-oxazolidin-2-one (II/ME) product was detected by gas chromatography (internal standard = hexadecane).

Control Experiments 1: Reaction of 2-Oxazolidinone with Phenylacetaldehyde under catalytic conditions. Following a procedure similar to that described above for the catalytic reactions, (PhCN)₂PdCl₂ (9.6 mg, 0.025 mmol), CuCl₂ (3.4 mg, 0.025 mmol) and 2-oxazolidinone (43.6 mg, 0.5 mmol) in DME (1 mL) were combined in a 13x100 mm disposable culture tube. After purging with oxygen and warming to 60 °C, phenylacetaldehyde (58.5 µL, 0.5 mmol) was added to the reaction mixture and the mixture was stirred for 24 h. GC analysis (internal standard = hexadecane) revealed only small amounts of 3-((E)-styryl)-oxazolidin-2-one (**I/aME**, 8%) in the reaction mixture, insufficient to account for product formation in the catalytic reaction.

Control Experiments 2. Oxidative Amination of Styrene with 2-oxazolidinone Under Anaerobic Conditions in the Presence of (MeCN)₂PdCl₂ (3). Following a procedure similar to that described above for the catalytic reactions, (MeCN)₂PdCl₂ (6.5 mg, 0.025 mmol) and oxazolidinone (43.6 mg, 0.5 mmol) were suspended in DME (2mL) in a 13x100mm disposable culture tube; however, the solution was purged with nitrogen at room temperature for ca. 30 min. Upon warming to 60 °C, styrene (0.34 mL, 3 mmol) was added to the reaction mixture and the reaction was stirred for 12 h under a nitrogen atmosphere (1 atm). Upon completion, the reaction mixture was immediately filtered through a pad of silica gel to remove the catalyst (eluted with ether) and solvent was removed from the resulting filtrate under reduced pressure. The residue was dried under vacuum and a 3.9% yield of 3-((E)-styryl)-oxazolidin-2-one (**I/aME**) was calculated by ¹H NMR spectroscopy versus Ph₃CH as internal standard.

Control Experiments 2. Oxidative Amination of Styrene with 2-oxazolidinone Under Anaerobic Conditions in the Presence of (Et₃N)₂PdCl₂ (4). Following a procedure similar to that described above for the catalytic reactions, (MeCN)₂PdCl₂ (6.5 mg, 0.025 mmol), Et₃N (7 µL, 0.05 mmol) and 2-oxazolidinone (43.6 mg, 0.5 mmol) were suspended in DME (2mL) in a 13x100 mm disposable culture tube; however, the solution was purged with nitrogen at room temperature for ca. 30 min. Upon warming to 60 °C, styrene (0.34 mL, 3 mmol) was added to the reaction mixture and the reaction was stirred for 12 h under a nitrogen atmosphere (1 atm). Upon completion, the reaction mixture was immediately filtered through a pad of silica gel to remove the catalyst (eluted with ether) and solvent was removed from the resulting filtrate under reduced pressure. The residue was dried under vacuum, and a 2.3% yield of 3-(1-phenylvinyl)-oxazolidin-2-one (**II/ME**) was calculated by ¹H NMR spectroscopy versus Ph₃CH as internal standard.

Single Crystal X-Ray Crystallography of (Et₃N)₂PdCl₂ (4).

Data Collection

A dark red crystal with approximate dimensions 0.43 x 0.32 x 0.26 mm³ was selected under oil under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 72 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 4194 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of $0.80 \text{ \AA}$. A total of 5235 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.⁴

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement.⁵

A successful solution by the direct methods provided most non-hydrogen atoms from the E -map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The Pd complex occupies a crystallographic inversion center.

The final least-squares refinement of 82 parameters against 1605 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0226 and 0.0606, respectively. The final difference Fourier map was featureless.

The ORTEP diagram is drawn with 50% probability ellipsoids.

Table S3. Crystal data and structure refinement for 4.

Identification code	sta08	
Empirical formula	C ₁₂ H ₃₀ Cl ₂ N ₂ Pd	
Formula weight	379.68	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 6.9798(17) Å b = 10.934(3) Å c = 10.495(3) Å	$\alpha = 90^\circ$. $\beta = 90.905(4)^\circ$. $\gamma = 90^\circ$.
Volume	800.8(3) Å ³	
Z	2	
Density (calculated)	1.575 Mg/m ³	
Absorption coefficient	1.476 mm ⁻¹	
F(000)	392	
Crystal size	0.43 x 0.32 x 0.26 mm ³	
Theta range for data collection	3.53 to 26.36°	
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -13 ≤ l ≤ 10	
Reflections collected	5235	
Independent reflections	1605 [R(int) = 0.0239]	
Completeness to theta = 26.36°	98.3 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.7001 and 0.5693	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1605 / 0 / 82	
Goodness-of-fit on F ²	1.047	
Final R indices [I > 2sigma(I)]	R1 = 0.0226, wR2 = 0.0597	
R indices (all data)	R1 = 0.0237, wR2 = 0.0606	
Largest diff. peak and hole	1.202 and -0.492 e.Å ⁻³	

Table S4. Bond lengths [Å] and angles [°] for 4

Pd-N(1)#1	2.1716(15) Å
Pd-N(1)	2.1716(15) Å
Pd-Cl(1)#1	2.3179(6) Å
Pd-Cl(1)	2.3179(6) Å
N(1)-C(3)	1.508(2) Å
N(1)-C(1)	1.508(2) Å
N(1)-C(5)	1.510(2) Å
C(1)-C(2)	1.518(3) Å
C(3)-C(4)	1.519(3) Å
C(5)-C(6)	1.529(3) Å
N(1)#1-Pd-N(1)	180.0 °
N(1)#1-Pd-Cl(1)#1	92.42(4) °
N(1)-Pd-Cl(1)#1	87.58(4) °
N(1)#1-Pd-Cl(1)	87.58(4) °
N(1)-Pd-Cl(1)	92.42(4) °
Cl(1)#1-Pd-Cl(1)	180.0 °
C(3)-N(1)-C(1)	106.96(13) °
C(3)-N(1)-C(5)	109.74(14) °
C(1)-N(1)-C(5)	109.03(13) °
C(3)-N(1)-Pd	107.21(10) °
C(1)-N(1)-Pd	109.91(10) °
C(5)-N(1)-Pd	113.76(11) °
N(1)-C(1)-C(2)	114.31(15) °
N(1)-C(3)-C(4)	113.07(15) °
N(1)-C(5)-C(6)	116.46(16) °